POLYETHERSULFONE/CLOISITE15A MIXED MATRIX MEMBRANES FOR GAS SEPARATION

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ABSTRACT

Fabrication of mixed matrix membrane (MMM) with superior gas transport properties is challenging due to the poor dispersion of the filler in the membrane and the complicated interaction of polymer-clay surface. The purpose of this study is to develop polymer-clay based MMM for carbon dioxide (CO_2) removal from methane (CH_4) and to study the effects of interface voids and clay dispersion on gas separation. Asymmetric flat sheet MMM from polyethersulfone (PES) and sonicated cloisite15A (C15A) clay particles was prepared by a controlled fabrication parameters and phase inversion technique. The impacts of adding C15A on the MMM properties were investigated by using morphological, structural, thermal, mechanical, functional group and performance analyses. In the first phase of the study, the effect of different loading of C15A was investigated. Significant changes on the membrane morphology and thermal stability were observed for the fabricated MMMs. At 1 weight% C15A loading (PES/C15A1), MMM showed the best gas transport properties with 37% and 100% improvement on CO_2 permeance and CO_2/CH_4 selectivity, respectively. For the second part of the study, the state of dispersion of the silicate layers in MMM was investigated by qualitative and quantitative analyses. Partial intercalated and exfoliated silicate layers in PES/C15A1 contributed to the enhancement of the membrane mechanical properties. The increase of tortuosity in MMM reduced the CH_4 permeance with a significant improvement for the CO_2/CH_4 selectivity from 22.57 to 46.89. Particle size measurement, particle density measurement and free-path spacing measurement also demonstrated that the dispersion state in PES/C15A1 was striking with the increase in aspect ratio, dispersed single silicate layers, particle density and evidence of several tactoid classes. It was discovered that high C15A loading (5 weight%) deteriorated the PES/C15A5 performance due to the interfacial voids. Hence in the third phase, C15A was functionalized with 3-aminopropyl triethoxysilane coupling agent. Selectivity improvement was observed on the modified-C15A MMM suggesting a better interaction between the clay surface and PES matrix. From this study, incorporation of C15A has shown great CO_2/CH_4 separation enhancement and can be regarded as potential filler for MMM.

ABSTRAK

Pembuatan membran campuran matrik (MMM) dengan sifat-sifat pengangkutan gas yang unggul adalah mencabar disebabkan penyerakan pengisi yang rendah dan kerumitan saling tindak antara permukaan polimer-pengisi. Tujuan kajian ini adalah untuk menghasilkan MMM berasaskan polimer-tanah liat untuk penyingkiran karbon dioksida (CO_2) daripada metana (CH_4) dan mengkaji kesan lompang antara permukaan dan penyerakan pengisi terhadap pemisahan gas. MMM kepingan rata tidak simetri dihasilkan daripada polietersulfona (PES) dan partikel tanah liat *cloisite15A* (C15A) disonikasi melalui parameter pembuatan terkawal dan teknik fasa-balikan. Kesan penambahan C15A terhadap sifat membran telah dikaji menggunakan analisa morfologi, struktur, terma, mekanikal, kumpulan fungsi dan prestasi. Pada fasa pertama kajian ini, kesan muatan C15A yang berbeza dalam penghasilan PES/C15A MMM telah dikaji. Perubahan yang ketara pada morfologi dan kestabilan terma dapat diperhatikan ke atas MMM yang dihasilkan. Pada 1% berat muatan C15A (PES/C15A1), MMM menunjukkan sifat pengangkutan gas yang terbaik dengan peningkatan penelapan CO_2 sebanyak 37% dan kememilihan CO_2/CH_4 sebanyak 100%. Pada fasa kedua kajian ini, keadaan penyerakan lapisan silikat dalam MMM dikaji dengan analisis kuantitatif dan kualitatif. Lapisan silikat yang separa interkalat dan terkelupas dalam PES/C15A1 menyumbang kepada peningkatan sifat mekanikal membran. Peningkatan kelikuan dalam MMM telah mengurangkan kadar penelapan CH_4 dengan meningkatkan kememilihan CO_2/CH_4 dari 22.57 kepada 46.89. Pengukuran saiz partikel, pengukuran ketumpatan partikel dan pengukuran jarak laluan-bebas juga menunjukkan bahawa keadaan penyerakan dalam PES/C15A1 adalah ketara dengan peningkatan dalam nisbah aspek, penyerakan lapisan silikat tunggal, ketumpatan partikel dan kehadiran kelas taktoid. Kajian ini mendapati kadar muatan C15A yang tinggi (5%) dalam PES/C15A5 boleh menyebabkan penurunan prestasi MMM akibat pembentukan lompang antara permukaan. Oleh itu, pada fasa ketiga, C15A telah difungsikan dengan agen gandingan 3-aminopropil trietoksilana. Peningkatan kadar kememilihan dapat diperhatikan pada MMM dengan C15A yang telah diubah suai menunjukkan interaksi yang lebih baik antara permukaan tanah liat dan matriks PES. Kajian ini menunjukkan, penggabungan C15A dengan PES telah menyebabkan peningkatan yang ketara dalam pemisahan CO_2/CH_4 dan C15A mempunyai potensi yang besar sebagai pengisi untuk MMM.

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LIST OF ABBREVIATIONS

APDEMS	-	3-aminopropyl-diethoxymethyl silane
APTES	-	3-aminopropyltriethoxysilane
AR	-	Aspect ratio
CH_4	-	Methane
CNT	-	Carbon nanotube
CMS	-	Carbon molecular sieve
CO_2	-	Carbon dioxide
CA	-	Cellulose acetate
C15A	-	Cloisite15A
C20A	-	Cloisite20A
C25A	-	Cloisite25A
C30B	-	Cloisite30B
DMAc	-	Dimethylacetamide
DSC	-	Differential scanning calorimetry
EDX	-	Energy dispersive x-ray
EtOH	-	Ethanol
FESEM	-	Field emission scanning electron microscopy
FPSM		Free path spacing measurements
FTIR-ATR	-	Fourier transform infrared spectroscopy attenuated total reflection
H_2	-	Hydrogen
HNT	-	Halloysite nanotube
HR-TEM	-	High resolution transmission electron microscopy
H_2S	-	Hydrogen sulphide
LR-TEM	-	Low resolution transmission electron microscopy
MeOH	-	Methanol
MMM	-	Mixed matrix membrane

MMT	-	Montmorillonite
MOF	-	Metal organic framework
MSS	-	Mesoporous silica spheres (MSSs)
MWCNT	-	Multiwall carbon nanotube
N_2	-	Nitrogen
NO_2	-	Nitrogen dioxide
NMP	-	n-Methyl-2-pyrrolidone
O_2	-	Oxygen
PCN	-	Polymer clay nanocomposite
PDM	-	Particle density measurements
PDMS	-	Polydimethylsiloxane
PEI	-	Polyetherimide
PES	-	Polyethersulfone
PI	-	Polyimide
PLLA	-	Poly(L-lactide)
PSf	-	Polysulfone
PSM	-	Particle size measurements
RTIL	-	Room temperature ionic liquids
SEM	-	Scanning electron microscopy
SO_2	-	Sulphur dioxide
TAP	-	2,4,6-triaminopyrimidine
TEM	-	Transmission electron microscopy
TFC	-	Twice functionalized organoclay
TGA	-	Thermogravimetric analysis
THF	-	Tetrahydrofuran
TiO_2	-	Titanium dioxide
WAXD	-	Wide angle x-ray diffraction
XRD	-	X-ray diffraction
ZIF-8	-	Zeolitic imidazolate framework

LIST OF SYMBOLS

A	-	Effective membrane area (cm^2)
AR_{av}	-	Average aspect ratio (dimensionless)
B	-	Interfacial interaction parameter (dimensionless)
d	-	Interlayer distance between the silicate layers (Å)
d_{clay}	-	Clay particle thickness (nm)
$D_{0.1}$	-	Free-path distance distribution (dimensionless)
$\frac{dV_i}{dt}$	-	Volumetric flowrate of gas permeated through the membrane (cm^3/s)
h	-	Gallery height of silicate layers for intercalated orientation (nm)
h_0	-	Gallery height of silicate layers for unmixed orientation (nm)
i	-	Gas penetrant *i* (dimensionless)
j	-	Gas penetrant *j* (dimensionless)
L_{av}	-	Average length of the clay tactoid (nm)
L_{clay}	-	Clay particle length (nm)
L_f	-	Free-space length (nm)
L_s	-	Square length (nm)
MW	-	Molecular weight of repeat unit of polymer (g/mol)
n	-	Order of diffraction in the calculation (dimensionless)
N	-	Number of silicate layers per tactoid (dimensionless)
N_{pi}	-	Number of silicate layers per tactoid (dimensionless)
p	-	Partial pressure (bar)
P		Permeance (GPU)
Tg	-	Glass transition temperature (°C)
t_{av}	-	Average thickness of the clay tactoid (nm)

Greek letters

Å	-	Angstrom
ρ	-	Density (g/cm^3)
σ_y	-	Yield of strength (MPa)
Φ_f	-	Volume fraction of the clay
λ	-	Wavelength of X-ray equal to 0.154056 nm
θ	-	Angle at the maximum point of the first peak in the XRD pattern (°)
α	-	Selectivity (dimensionless)
$\epsilon_{\|\|}$	-	Interparticular distance parallel to tactoids orientation (nm)
$\epsilon_{\perp}$	-	Interparticular distance perpendicular to tactoids orientation (nm)
μ	-	Mean spacing (nm)
Δp	-	Transmembrane pressure drop (bar)
ξc_{lay}	-	Correlation length (nm)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Concentrated efforts in developing new technologies for carbon dioxide (CO_2) removal from various sources such as fossil fuel based power plant, either from pre-combustion or post combustion processes, landfill gas, natural gas or other gas mixtures containing CO_2 and methane (CH_4) have been made since the last few decades [1,2]. Although CH_4 is the majority component in natural gas (75%-90%), it also contains ethane, propane, butane, and other hydrocarbons along with undesirable impurities such as water, CO_2, nitrogen (N_2) and hydrogen sulphide (H_2S). In addition, removal of CO_2 from natural gas is important because of its corrosive effects towards the gas pipelines and to increase the calorific value and transportability of the natural gas [3,4].

Sweetening of natural gas is commonly carried out by chemical and physical treatment or combination of both by alkanolamine sweetening, carbonate and water washing, rectisol, selexol, sulfinol, molecular sieve adsorbent and activated carbon [5]. Although this conventional methods have been widely used, they provide several disadvantages such high operating cost, low removal capacity, complex process, high equipment corrosion, high energy consumption during solvent regeneration and absorption of metallic trace components such as mercury [6–8].

Natural gas is considered as an important source of fuel, as well as a primary feedstock with different component of valuable precursors for most petrochemical industries. Thus, the demand for economical, sufficient energy with good quality and environmental sustainability has attracted many researchers until now to find the viable technology in treating the natural gas. In view of this issue, other alternative to purification of natural gas other than the conventional methods used is attempted to explore the potentials and benefits. Membrane-based technology revolutionized the gas separation industry due to the simplicity of the membrane gas separation and its energy efficiency [9]. Today, membrane technology for gas separation is a well-consolidated technique and in comparison with the conventional techniques, it has proven to be a promising substitute. However, for a membrane to be useful for the CO_2 removal, characteristics such as high permeability and selectivity, thermal and chemical stability, plasticisation resistance, aging resistance, cost effective and modularity are important to achieve the desired separation [10].

1.2 Problem Statement

The membrane used in gas separation can be classified into two categories; polymeric and inorganic membrane. Polymeric membranes, usually in the form of flat sheet or hollow fibres are capable of achieving moderate permeability and selectivity, with lower cost and easy manufacturing processes [11]. While these membranes have been the interest in gas separation industries [12,13], limitation such as performance trade-off revealed as Robeson upper-bound relationship has been one of the underlying reason for its slow growth for commercialization [14,15]. Also, these membranes are not able to withstand higher temperatures and rigorous environments thus requiring a pre-treatment of the natural gas if it is to be applied in petrochemical industries. Additionally, plasticization can occur if the polymers are exposed to hydrocarbons or CO_2 at high pressure, a typical operating condition for gas industries which results a reduction in the selectivity [16,17].

Inorganic membranes (metal, zeolite, ceramic, carbon), on the other hand, offers exceptional gas separation properties and has the ability to operate in aggressive physical and chemical environment with a better stability at higher temperature compared with those polymeric membranes [11]. However, these membranes suffer from manufacturing issues such as low reproducibility, mechanical resistance and breakability, high cost, and poor intensification [18]. During the last two decades, successful attempts in fabricating polymeric membrane surpassing the trade-off line is hindered due to the limitations possessed by the membrane itself. Similarly, inorganic membrane is not an alternate solution due to the issue of fragility. Hence, a new membrane with a better separation properties and improved thermal stability and mechanical strength is needed to fully utilize the potential of this technology in gas separation.

An emerging technology in membrane gas separation known as mixed matrix membranes (MMMs) is facilitated by the demand in membrane with desirable properties and most importantly, improved separation performances. MMMs are made from polymeric material by dispersing the nano or micro particles of inorganic fillers for example silica, carbon molecular sieves (CMS), zeolites, carbon nanotubes (CNTs), metal organic frameworks (MOFs), and clay into the continuous phase [15,19–22]. MMMs combine the advantages of each phase, which provide better physical, mechanical, thermal characteristics with the fillers acting as gas barrier during separation [3,14,23]. Furthermore, the inherent superior separation characteristics of the inorganic fillers through sieving like mechanism and tortuosity effect improved the barrier properties of MMMs. For this study, the ability for the organoclay to disperse well and its intercalated and exfoliated nature provides a more difficult path for the gas. Particle perturbation of polymer chain, free volume, CO_2 cylindrical shape, location of filler and nanogaps contributed to the increase of CO_2 permeance and reduction of CH_4 permeance. As a result, the addition of organoclay may enhance the selectivity of the MMMs relative to the existing polymeric membrane.

Since mixed matrix combines the polymeric material and inorganic filler, designing MMMs is often complicated by the interaction and compatibility between

the two materials. It is known that the rate of progress in understanding the polymeric membranes is well developed compared to the MMM; hence data for separation properties for polymers are readily available to the extent that further exploration by using this material in MMM is appealing. Despite the recent advancement in MMM, the challenge in developing the ultra-thin selective skin layer without introducing defects that could hindered gas separation remains unsolved. Further understanding on the compatibility of the polymer-particle interface is also necessary to avoid the morphological complexities related to MMM namely void and agglomeration of particles.

Extensive attention has been given to the development of MMM with wide choices of fillers for gas separation and most of the works are focusing on the effect of different loadings, fabrication parameters, surface modification, and structural defects due to the poor interaction between fillers and polymer. However, very few has emphasized in details on the role of the fillers in governing the gas path within the membrane. Therefore, in this study, attempts are made to investigate the potential of Cloisite15A (C15A) as filler for MMMs from polythersulfone (PES) and the changes on the overall membrane characteristics (i.e. morphology, thermal, mechanical) which influence the CO_2/CH_4 separation properties (i.e. permeance, selectivity). C15A was chosen as the inorganic filler due to its high aspect ratio, high surface area, improved *d*-spacing and easily available [24]. Meanwhile, PES has a good stability, considerable performance, commercially available and widely used in the literature [25]. Furthermore, investigation on PES embedded with C15A has never been reported in the literature. In addition, it is worth discussing two main factors correlating the morphological properties for an ideal separation: (1) the role of intercalation and exfoliation of the silicate layers in determining the gas path during the separation and (2) the extent of polymer-clay interaction at the surface of clay in the presence of interface voids with unmodified and modified clay with 3-aminopropyiltriethoxysilane (APTES). Fundamental understanding on these factors is crucial to design MMMs with improved performances in order to exploit the potential of this technology.

1.3 Objectives of the Study

Based on the problem statement discussed previously, the objectives of this study are outlined as follows:

i. To determine the effect of C15A incorporation as inorganic filler for flat sheet asymmetric PES MMMs in terms of the morphological, thermal stability, mechanical strength and gas separation performance.

ii. To determine the influence of silicate layers dispersion (intercalation and exfoliation) on the overall morphology and mechanical strength of the MMMs and the correlations with the gas separation with both qualitative and quantitative analysis

iii. To determine the effect of C15A modification with coupling agent, APTES on reducing the interface voids and improving the overall MMMs properties (i.e. morphological, thermal stability, mechanical strength) and gas separation performance.

1.4 Scopes of the Study

In order to achieve the above objectives, the following scopes of study have been performed:

i. Fabricating asymmetric flat sheet neat PES membranes through dry/wet induced phase inversion process by immersion precipitation technique with a fixed solution composition consisting PES/n-methyl-2-pyrollidone (NMP)/ethanol (EtOH).

ii. Preparing the asymmetric flat sheet MMMs PES/C15A by varying the clay concentration in the dope solution (1 and 5 wt% per total polymer) by using similar solution composition in the neat PES membranes.

iii. Surface modification of C15A with silane coupling using APTES in order to fabricate twice functionalized organoclay (TFC).

iv. Preparing the asymmetric flat sheet PES/C15A MMMs by using unmodified and silane modified C15A at clay concentration of 0.25 wt% (per total polymer) and fixed solution composition.

v. Characterizing membranes morphological structure, C15A dispersion and modification by using scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), fourier transform infrared spectroscopy attenuated total reflection (FTIR-ATR), X-ray diffraction (XRD) and energy dispersive X-ray (EDX).

vi. Characterizing physicochemical properties of membranes in terms of tensile strength, elongation at break, thermal degradation properties and glass transition temperature (*T*g) by using mechanical test, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

vii. Preparing sample for transmission electron microscopy (TEM) by using ultramictoromy for asymmetric flat sheet PES/C15A MMMs for different clay concentration (1 and 5 wt% per total polymer).

viii. Characterizing intercalated and exfoliated structure of silicate layers in PES/C15A MMMs in terms of qualitative analysis by using TEM, wide angle X-ray diffraction (WAXD), mechanical test and gas permeation.

ix. Characterizing intercalated and exfoliated structure of silicate layers in asymmetric flat sheet PES/C15A MMMs in terms of quantitative analysis by using particle size measurements (PSM), particle density measurements (PDM), free path spacing measurements (FPSM).

x. Evaluation of the permeation properties of the flat sheet membranes for CO_2/CH_4 separation based on the effects of different filler loadings (1 and 5 wt% per total polymer) and modification with APTES (0.25 wt% per total polymer) at a fixed operating conditions.

1.5 Rational and Significance of the Study

This study is expected to provide a better understanding on the underlying principle of fabrication of MMMs for gas separation by considering the morphological, physicochemical changes and gas separation of the membranes by the addition of inorganic filler. It is acknowledged that nanocomposites embedded with nanoclay have been used in various applications as reinforcement materials, electrical conductors, food packaging and fire retardant materials, however little attention has been given on their application as gas barriers. Therefore, attempts are made to investigate the potential of organoclays as fillers in MMMs through the incorporation of C15A into PES for CO_2/CH_4 separation. By identifying the ideal characteristics of the clay loadings, dispersion of silicate layers and interfacial behaviours of the filler, high performance MMMs can be fabricated. Besides, modified technique for ultramictromy of membrane was carefully conducted to obtain the required micrographs at the skin layer during TEM observation. Meanwhile, the increase in *d*-spacing after surfactant modification has enabled the material to intercalate and exfoliate within the polymer matrix and this is a unique characteristic of the filler. Therefore, to the best of our knowledge, no study has been conducted so far to correlate the effect of intercalation and exfoliation of silicate layers with the gas separation properties of the MMMs. While clay modification has been the interest of many researchers, the application of the resulted material has also

not being emphasized, especially in the gas separation. Therefore, the effect of silane modifier on issues particularly relating to the interfacial voids within the MMMs was also investigated. Advances in the development of MMMs could provide better alternative to stimulate the gas separation industries, particularly for natural gas sweetening process.

1.6 Organization of the Thesis

The thesis consists of 7 chapters. Chapter 1 describes the brief information concerning the gas separation industries, challenges with the current membrane technologies and an introduction of MMMs. In addition, the problem statements, objectives and scopes of the study have also been provided in this chapter.

Chapter 2 provides background information relevant to the gas separation technologies and their limitation as well as the past and current works on the development of membrane as a new approach for higher permeance and selectivity. Furthermore, the challenges and factors during fabrication of MMMs are also discussed. An introduction of polymer – clay nanocomposites technology and its application are also reviewed. Meanwhile, Chapter 3 includes a comprehensive experimental methods and characterization techniques used throughout the study.

Chapter 4 describes the preparation of the MMM through phase inversion techniques with a fixed composition of ternary system consisting PES, NMP, EtOH suspended with C15A (1 and 5 wt%). The membranes were characterized using SEM to determine the morphological properties and dispersion of clay on the surface and cross-section. Other membrane properties such as thermal stability, the amorphous nature and relationship of the changes of the solution viscosity on the formation of skin layer are discussed in this chapter. Detailed explanations on the effect of the clay addition, intercalation and exfoliation of silicate layers on the performance of MMMs as well as the comparison with the literatures are also given. The permeance

and selectivity of the fabricated membranes are also explained in terms of the morphological diagrams.

Chapter 5, on the other hand, provides an in-depth discussion on the potential of intercalation and exfoliation of silicate layers nanostructure and the consequence of these ultrafine distributions in relation to the MMMs higher gas barrier properties. Thus, the MMMs nanostructure were evaluated by qualitative analysis (TEM, WAXD, mechanical test, and gas permeation test) to correlate that the different silicate layers dispersion caused changes to the membrane properties hence the different gas separation behavior. Subsequently, characteristics parameters of clay tactoid were also investigated using quantitative analysis (PSM, PDM, FPSM) in terms of average thickness and length of the clay tactoid, average aspect ratio, interparticular distance parallel and perpendicular to the tactoids orientation, particle density and characteristics length of particle-free domain.

Since the distance of the interfacial gaps was also found to affect the performance of the MMMs, another attempt was made in the subsequent study to solve this issue. Chapter 6 presents the effect of aminosilane modification on the surface of C15A on the formation of PES/C15A MMMs in terms of morphological, physicochemical, and gas separation properties. Prior to the membrane fabrication, TFC was prepared by reacting APTES with C51A. Subsequently, physical and chemical properties of the TFC were first investigated in this chapter. Furthermore, all the prepared MMMs made of unmodified and modified clay was characterized and tested for specified operating conditions during gas permeation.

Finally, the general conclusions of the findings and some recommendations based on this study are provided in Chapter 7.

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